

Tank 5 Corrosion Studies



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Outline

- Background
- In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process
- Direct Measurement of Hydrogen Generation during Coupon Immersion Tests (Irradiated)
- Corrosion Mechanism Studies

Background

- Previous corrosion studies on carbon steel corrosion exposed to oxalic acid.
 - Coupon tests at expected chemical cleaning conditions (e.g., SRS Tank 16 and West Valley).
 - Based on these studies, a 100 mpy corrosion rate was expected for the chemical cleaning process at SRS.
 - If it is assumed that for each mole of iron dissolved one mole of hydrogen evolves, unacceptably high hydrogen generation rates would occur.

Background

- Unexplored variables
 - Presence of sludge
 - Presence of other anions in solution
 - Pre-existing oxides on the carbon steel surface
 - Aerated vs. de-aerated conditions
 - Coupon surface orientation
 - Irradiation
- Limitations of Previous Testing
 - Only one instance of a direct measurement of hydrogen generation during a corrosion coupon test.
 - Corrosion rates were performed over predetermined intervals (i.e., no instantaneous corrosion rate or hydrogen generation rate data).

In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

- Purpose
 - Monitor Open Circuit Potential (OCP)
 - Monitor Instantaneous Corrosion Rates
- Coupons
 - Carbon Steel (Initially Polished or Pre-corroded); For the first two experiments coupon was in the initially polished condition.
 - Horizontally mounted coupon and vertically mounted coupons to simulate tank bottom and tank wall, respectively.
- Techniques
 - Utilized a potentiostat to perform measurements.
 - Open Circuit vs. Time
 - Linear Polarization Resistance (LPR)

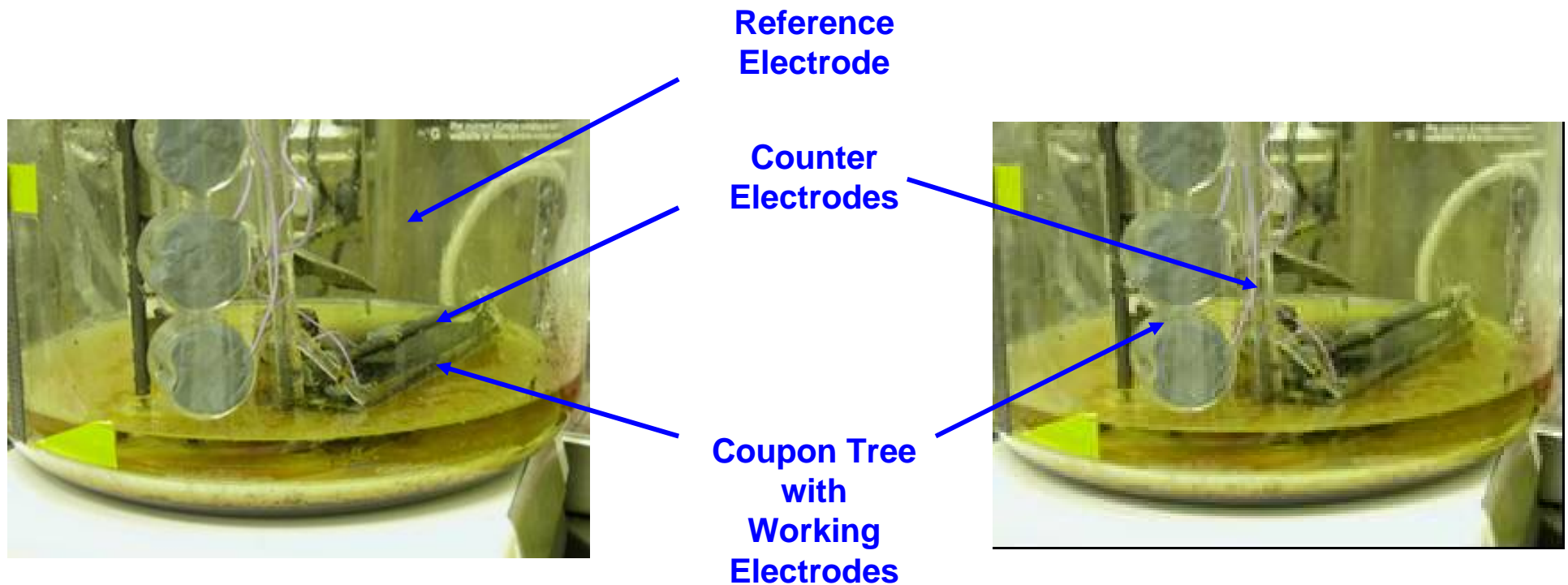


Vertically Mounted



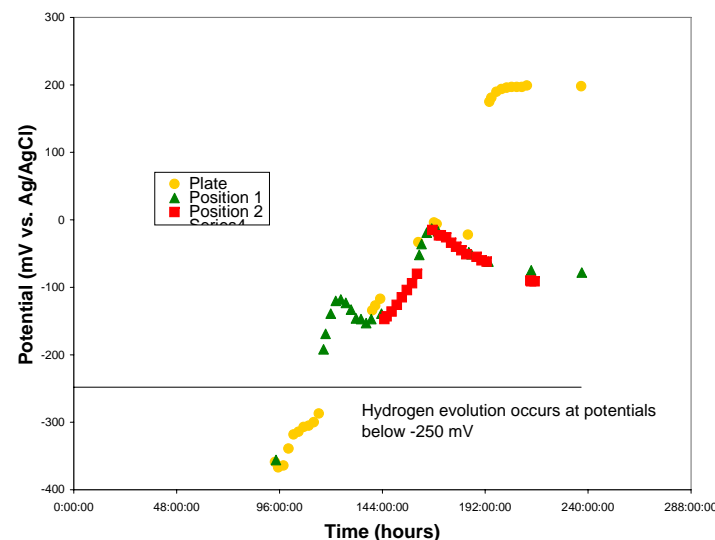
Horizontally Mounted

In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

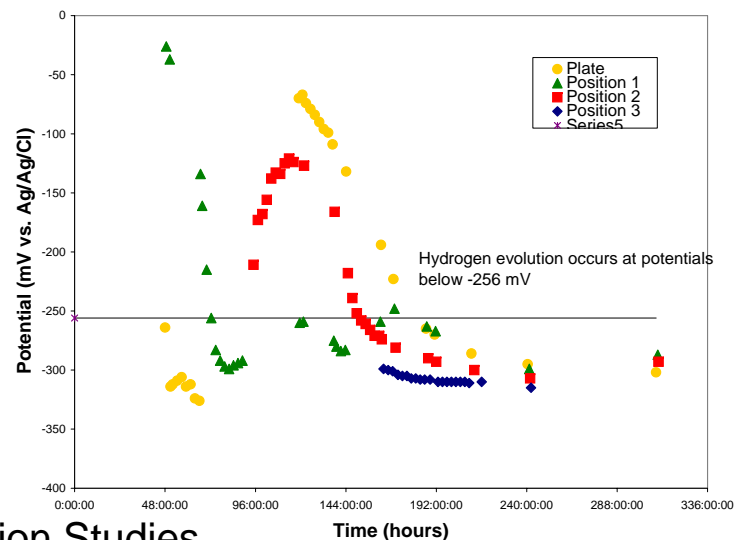


In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

- Open Circuit Potential vs. time for 8 wt % oxalic acid + sludge
- At 75 °C, hydrogen generation is not expected after the early stages of the process.
- At 25 °C, hydrogen generation is likely during the latter stages of the process.
- Hydrogen generation was measured concurrently. Little or no hydrogen generation was observed.



75°C

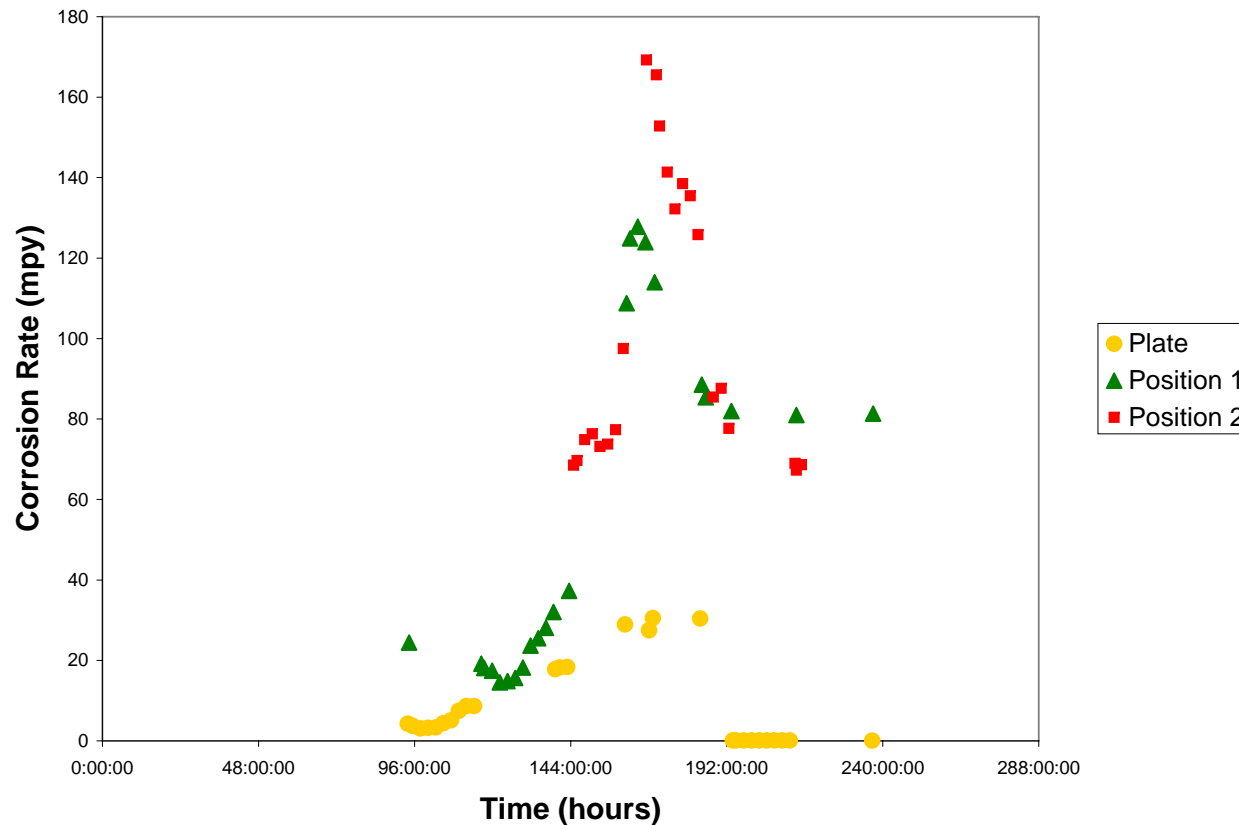


25°C

Tank 5 Corrosion Studies

In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

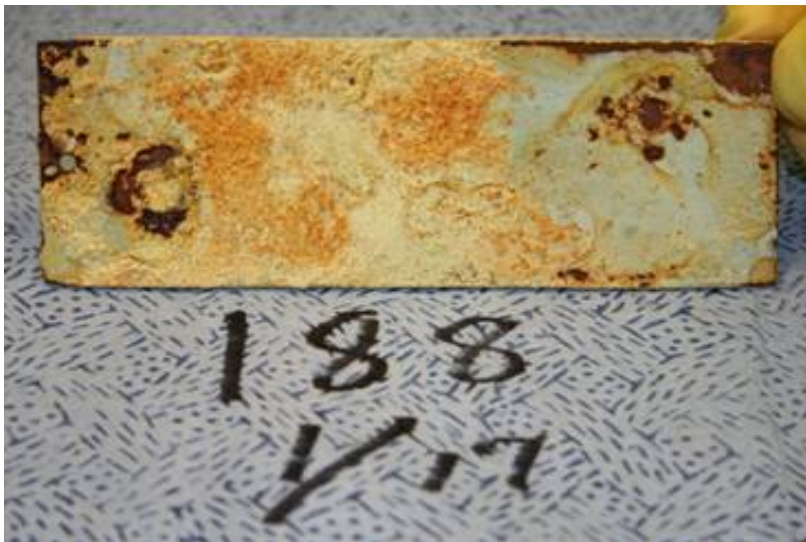
- The corrosion rates for vertically and horizontally oriented coupons.
- 8 wt % Oxalic Acid + sludge at 75 °C



Tank 5 Corrosion Studies

In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

- Significant build-up of ferrous oxalate on horizontal coupon.
- Immersed coupons have iron oxides as well as ferrous oxalates.
- Vertical coupon in vapor space contained iron oxides with no ferrous oxalates.



Post-test photo of horizontal plate from Test 2 (75 °C, mixed).



Post-test photo of vertical coupons from Test 4 (50 °C, unmixed).

In-situ Corrosion Monitoring during Simulation of the Chemical Cleaning Process

- Measured corrosion rates for the process demonstrations using simulated Tank 5F sludge depended on temperature, agitation and orientation of the coupon.
- Visual examination of the coupons at the completion of the tests showed evidence of general corrosion and pitting on the immersed coupons. General corrosion, but no appreciable pitting, occurred on the vapor space coupons without any evidence of acceleration due to oxalic acid in the vapor space.

Vertical Coupons

<u>Temperature (°C)</u>	<u>Corrosion Rate (mpy ±50%)</u>	
	<u>Mixed</u>	<u>Unmixed</u>
25	40	11
50	30	24
75	86	36

Horizontal Coupons

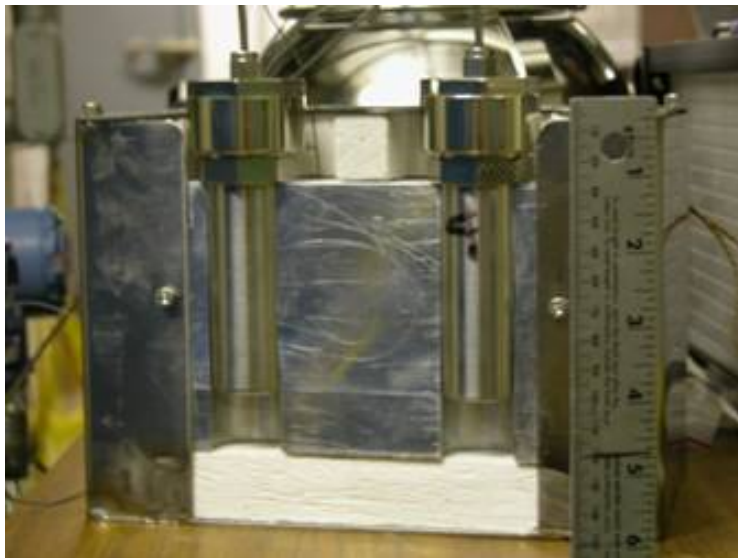
<u>Temperature (°C)</u>	<u>Corrosion Rate (mpy ±50%)</u>	
	<u>Mixed</u>	<u>Unmixed</u>
25	0.5	0.87
50	5	0.23
75	15	0.49

Direct Measurement of Hydrogen Generation

- Purpose:
 - Perform corrosion coupon test in a radiation environment to determine if radiation environment influences the overall rate of hydrogen evolution.
- Conditions
 - Pre-corroded carbon steel coupon.
 - Radiation field of 25,000 rads/hr
 - 1 ml of sludge and 15 ml of 8 wt % oxalic acid.
 - Approximately 30 ml of vapor space in test vessel.
 - Control tests in non-irradiated environment were performed.

Direct Measurement of Hydrogen Generation

- Components of Test Set-up



Test Vessel in Heating Block

Cobalt Source

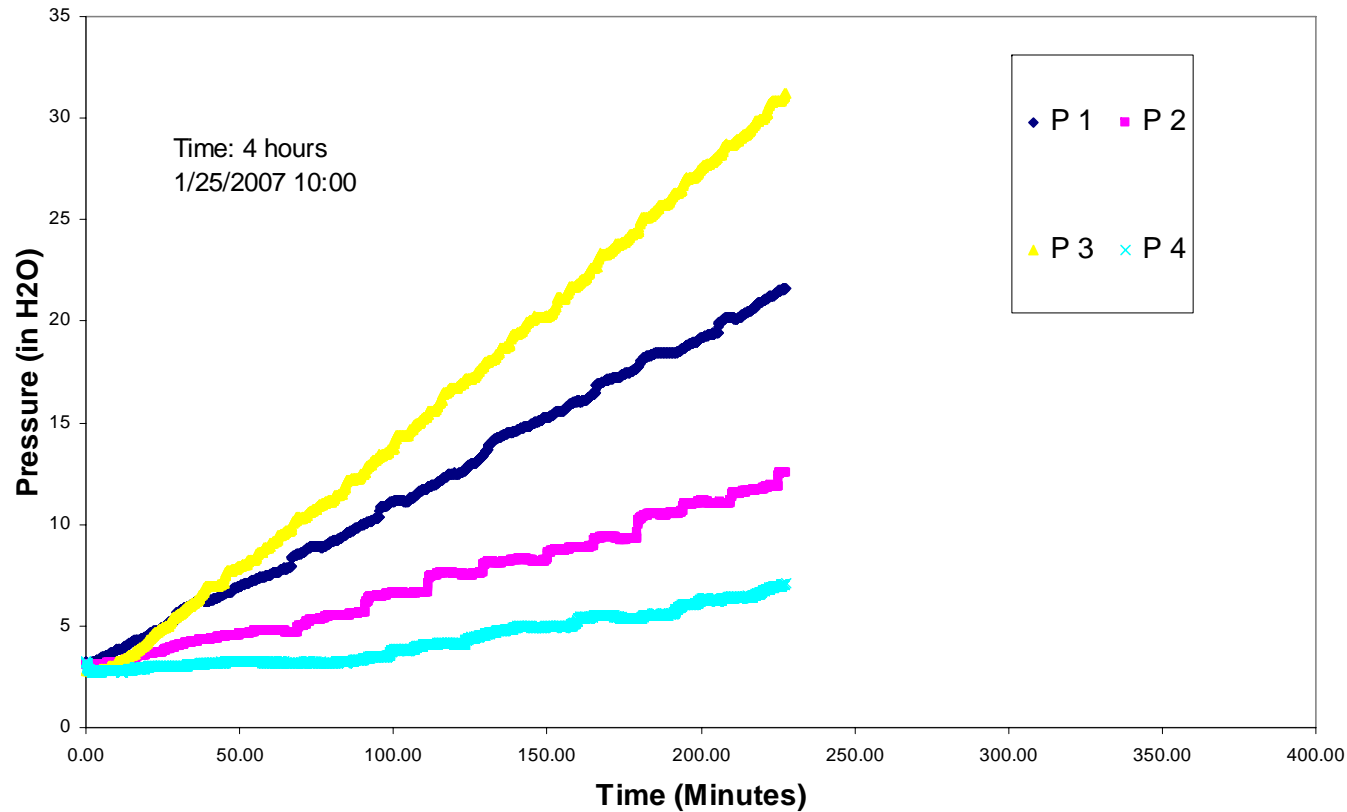


Sample Manifold and GC



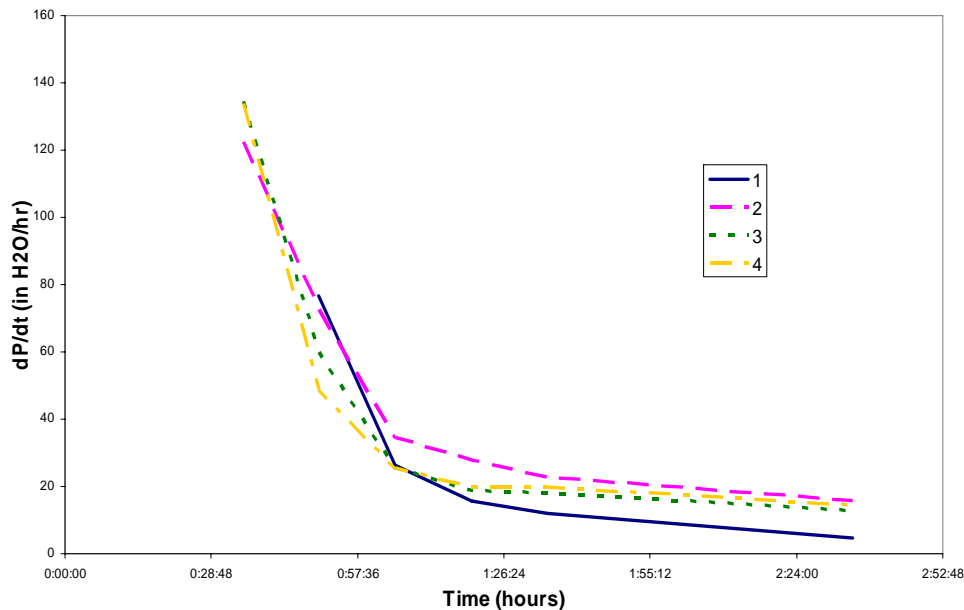
Direct Measurement of Hydrogen Generation

- Pressure build-up as a function of time.
- Tests 1 and 3 were in irradiated environment, while Tests 2 and 4 were in non-irradiated environment.

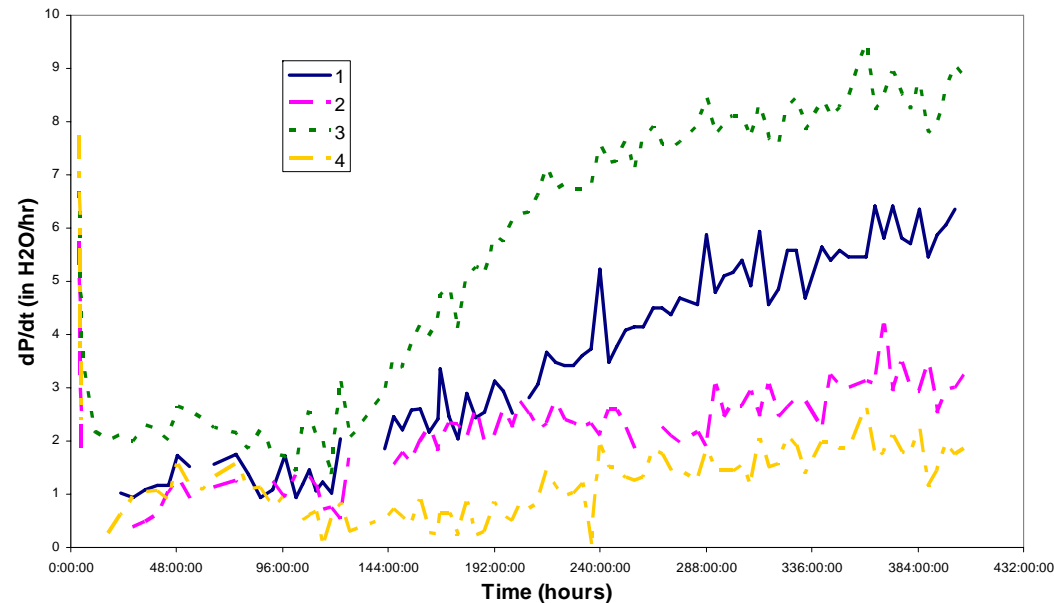


Direct Measurement of Hydrogen Generation

- Test at 50 °C; irradiated (P1 and P3) and non-irradiated (P2 and P4).
- Initially very high gas generation rates; No effect of radiation. Primary component of the gas was carbon dioxide.
- Irradiation contribution to hydrogen generation was observed to be small.
- Hydrogen generation rates were the greatest for the 50 °C tests.



Initial 3 hours



After 3 hours

Direct Measurement of Hydrogen Generation

- The maximum time-averaged corrosion rates tests in the presence of radiation were 15 mpy, 60 mpy, and 12 mpy for the 25, 50 and 75 °C tests, respectively.
- The irradiated tests generated markedly more hydrogen, but comparable total gas, at the higher temperatures (i.e., 50 °C and 75 °C) than observed in the process demonstrations and actual waste tests. The irradiation test method included pulling vacuum on the sample containers and we believe this approach de-gassed the liquid removing oxygen. The absence of oxygen prevented formation of protective oxide solids observed in other experiments as confirmed by x-ray diffraction of coupons.
- Since the process demonstrations with simulant involved comparable mixing energies and ventilation conditions as the planned operations, the authors select these results as representative of planned operations.

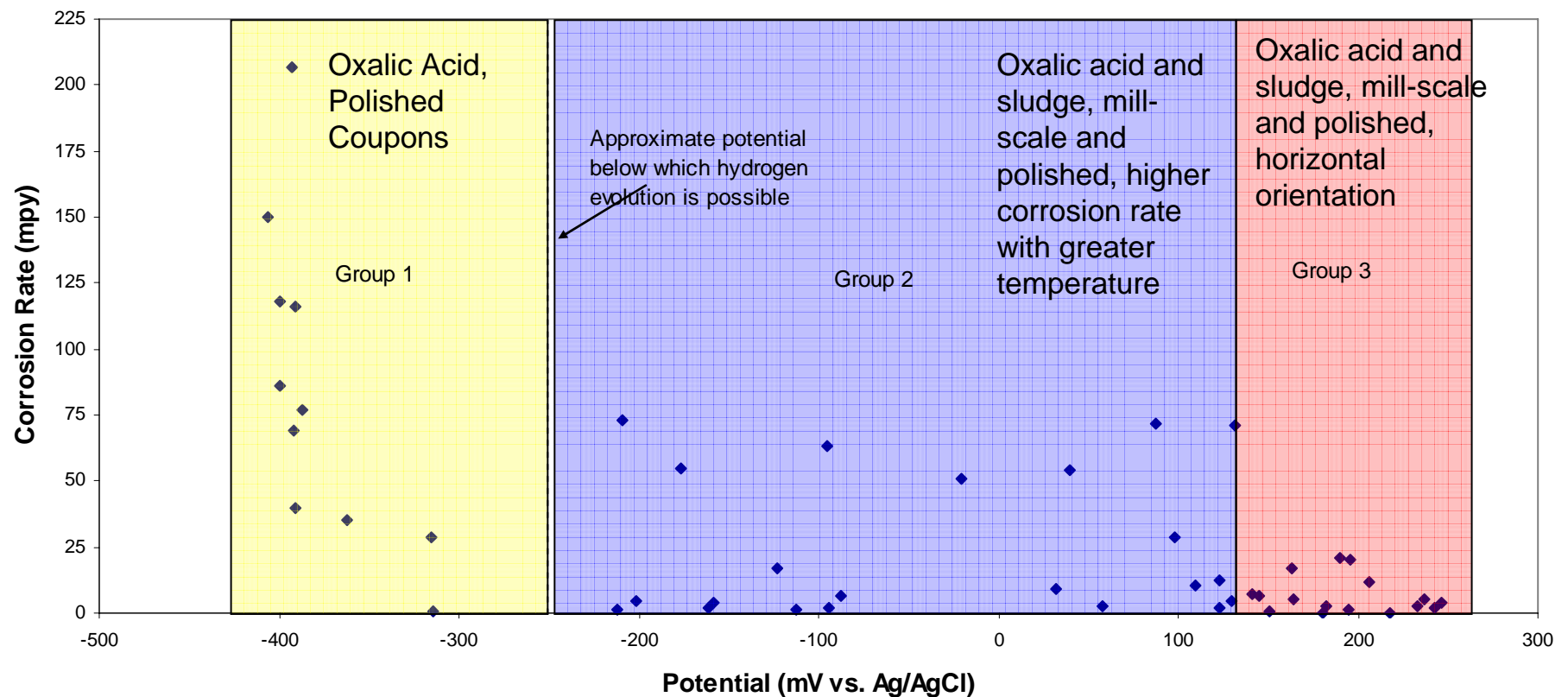
Corrosion Mechanism Studies

- Purposes
 - Use electrochemical techniques to investigate the corrosion mechanism.
 - Define environmental variables that impact corrosion and the rate of hydrogen generation.
 - Explain observations from process demonstrations
- Techniques
 - Open circuit potential vs. time
 - Linear polarization resistance
 - Cathodic potentiodynamic polarization
 - Anodic potentiodynamic polarization

Corrosion Mechanism Studies

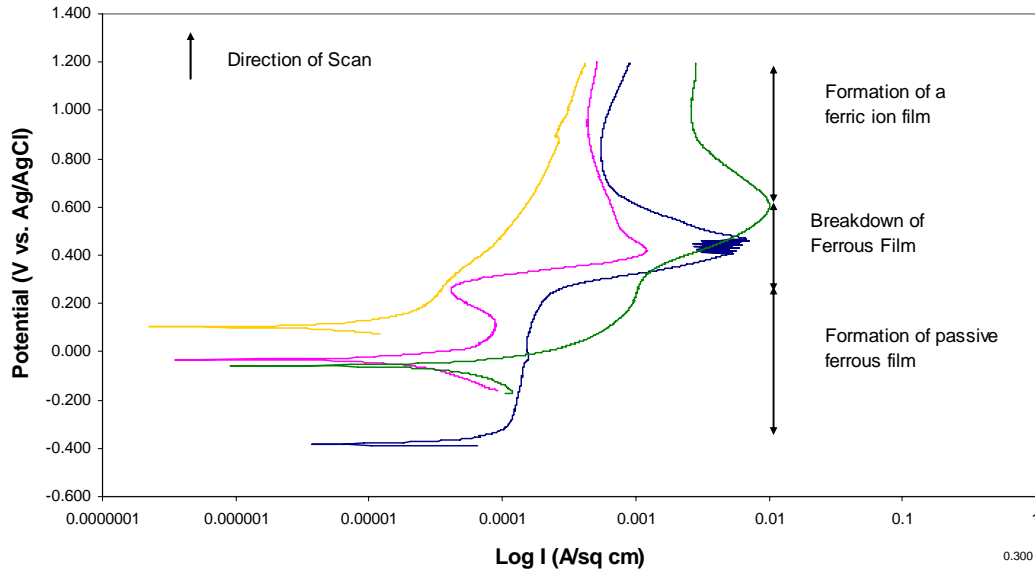
- Environmental Variables
 - Temperature
 - Surface Orientation
 - Agitation
 - Light
 - Oxalic Acid vs. Oxalic Acid + Sludge
 - Aerated vs. De-aerated
- Materials
 - Polished vs. Pre-corroded samples

Corrosion Mechanism Studies



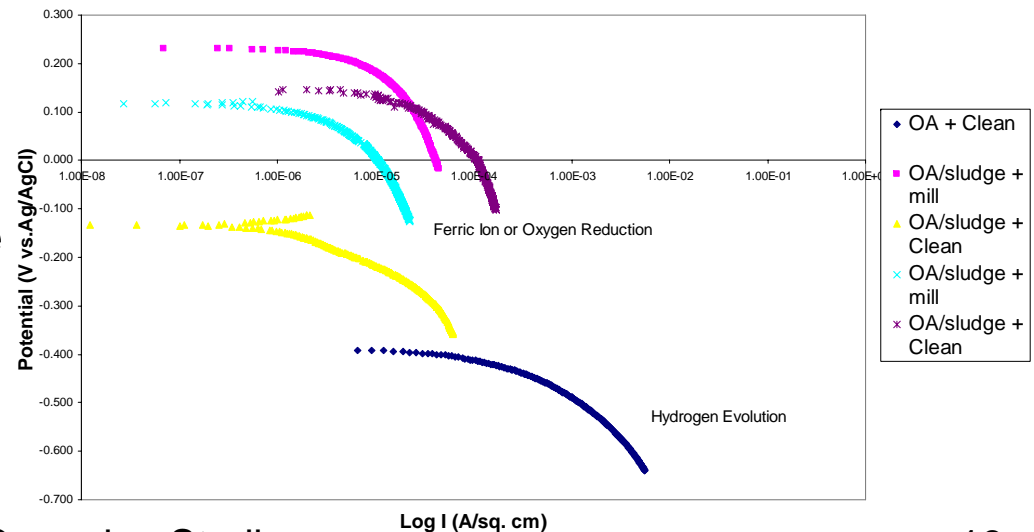
Distribution of open circuit potential and corrosion rates for the electrochemical tests.

Corrosion Mechanism Studies



General behavior for the anodic polarization curves.

General behavior for the cathodic polarization curves.



Corrosion Mechanism Studies

- The dominant cathodic reaction was hydrogen evolution in tests in oxalic acid solutions on polished coupons.
- The addition of sludge simulant to the test changed the active cathodic reaction from hydrogen evolution to either oxygen reduction or ferric ion reduction.
- The ferric ion reduction reaction was dominant in high temperature solutions (50°C and 75°C) where oxygen solubility was low and ferric ion solubility was high.
- The oxygen reduction reaction was dominant at the low temperature (25°C) where oxygen solubility was high and ferric ion solubility was low.
- De-aerated conditions favor either the ferric ion reduction or hydrogen evolution cathodic reactions.

Conclusions

- Measured corrosion rates for the process demonstrations using simulated Tank 5F sludge depended primarily on temperature, agitation and orientation of the coupon.
- The presence of sludge and the mill-scale on the coupon shifts the potential into a region where hydrogen evolution is unlikely.